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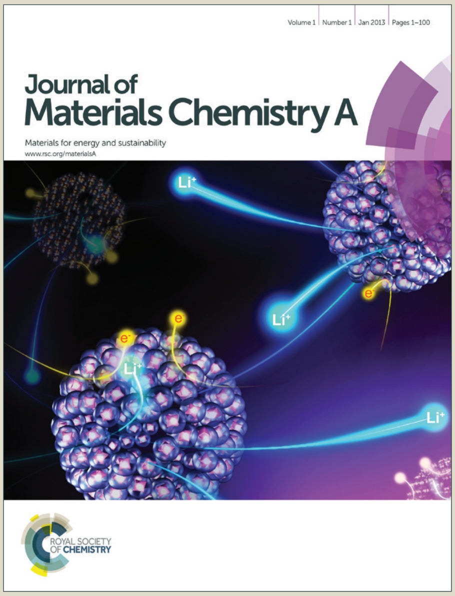

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ARTICLE TYPE

Development of D-π-A dye with benzothienopyridine as electron-withdrawing anchoring group for dye-sensitized solar cells

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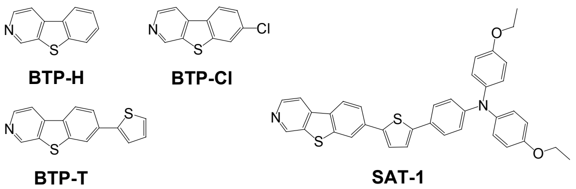
D–π–A dye SAT-1 with benzo[4,5]thieno[2,3-*c*]pyridine as electron-withdrawing anchoring group capable of forming a hydrogen bonding at the Brønsted acid sites or a coordinate bonding at the Lewis acid sites on TiO_2 surface has been developed as a new-type of D-π-A dye sensitizer for dye-sensitized solar cells.

Dye-sensitized solar cells (DSSCs) based on dye sensitizers adsorbed on nanocrystalline TiO_2 electrodes are of considerable scientific and practical interest from the viewpoint of their interesting construction and operational principles, colorful and decorative nature, and low cost of production.[1–8] To develop high-performance DSSCs, many kinds of donor–acceptor π-conjugated (D–π–A) dyes possessing both electron-donating (D) and electron-withdrawing anchoring (A) groups linked by π-conjugated bridges, possessing broad and intense absorption spectral features, have been designed and developed so far, and would be especially expected to be one of the most promising classes of organic dye sensitizers.[3–9] Recently, to create more effective D–π–A dye sensitizers, many researchers focused on the design and synthesis of new types of D–π–A dye sensitizers with electron-withdrawing anchoring groups such as the nitro group,[9] aldehyde,[10] and 2-(1,1-dicyanomethylene)rhodanine,[11] pyridine,[12] and 8-hydroxylquinoline[13] as an alternative to conventional carboxyl groups. In our previous work, we found that a new type of D–π–A dye sensitizers with a pyridyl group as an electron-withdrawing–injecting anchoring group were predominantly adsorbed on the TiO_2 film through coordinate bonding between the pyridyl group of the dye and the Lewis acid site (exposed Ti^{n+} cations) on the TiO_2 surface.[12a, b] It was demonstrated that a new type of D–π–A dye sensitizer can inject electrons efficiently from the pyridyl group to the conduction band (CB) of the TiO_2 electrode through coordinate bonding, rather than the bidentate bridging linkage between conventional D–π–A dye sensitizers with carboxyl groups and the Brønsted acid sites (surface-bound hydroxyl groups, Ti–OH) on TiO_2 surface. More recently, we have found that the D–π–A dye sensitizer with two pyridyl groups is predominantly adsorbed on the TiO_2 surface through hydrogen bonding at Brønsted acid sites.[12c] In addition, the photovoltaic performances of DSSCs based on D–D–π–A organic dyes and a series of porphyrin-based dyes with pyridyl groups were reported by Zheng et al.[12e] and Coutsolelos et al.[12f], respectively. However, to provide a direction in molecular design toward creating efficient D–π–A dye sensitizers with pyridyl groups, further fundamental studies to obtain useful knowledge about not only the biding mode of the dyes on the TiO_2 surface but also the influences of the binding modes on the photovoltaic performances of DSSCs are therefore necessary.

Therefore, in this work, we have designed and synthesized D–π–A dye **SAT-1** with thiophene-fused pyridine ring, benzo[4,5]thieno[2,3-*c*]pyridine[14] as electron-withdrawing–anchoring group (Scheme 1; see Scheme S1 in ESI† for the detailed synthetic procedures). In addition, to investigate the influences of substituent on the biding mode of benzo[4,5]thieno[2,3-*c*]pyridine derivatives, we have synthesized **BTP-H** without a substituent, **BTP-Cl** with chloride atom as an electron-withdrawing substituent and **BTP-T** with a thiophene ring as an electron-donating substituent. It was found the dye **SAT-1** is predominantly adsorbed on the TiO_2 surface through the hydrogen bonding at Brønsted acid sites, whereas the benzo[4,5]thieno[2,3-*c*]pyridine derivatives are predominantly adsorbed on the TiO_2 surface through coordinate bonding at Lewis acid sites. Here we reveal the influences of interaction between the pyridyl group of the dye and TiO_2 surface on the photovoltaic performances of **SAT-1**.



Scheme 1 Chemical structures of dye sensitizer **SAT-1** and benzo[4,5]-thieno[2,3-*c*]pyridine derivatives **BTP-H**, **BTP-Cl** and **BTP-T**.

The absorption and fluorescence spectra of **SAT-1** in THF are shown in Fig. 1a. A strong absorption band with absorption peak wavelength at 408 nm is assigned to the intramolecular charge transfer (ICT) excitation from the electron donor moiety (triphenylamine) to the electron acceptor moiety (benzothienopyridine). The molar extinction coefficient (ε) for the ICT band is 56400 M^{-1} cm^{-1}. The corresponding fluorescence maximum (λ_{fl}^{max}) occurs at 500 nm, and the fluorescence quantum yield (Φ_{fl}) is 0.80. The MO calculations (AM1, INDO/S) indicate that the longest excitation band is mainly attributable to the transition from the HOMO to the LUMO, where the HOMO is mostly localized on the triphenylamine moiety containing a thiophene ring, and the LUMO is mostly localized on the benzothienopyridine moiety containing a thiophene ring (Figs. 2a, b). The changes in the calculated electron density accompanied by the first electron excitations for **SAT-1** reveal a strong ICT nature from the triphenylamine moiety to the benzothienopyridine moiety upon photoexcitation (Fig. 2c).

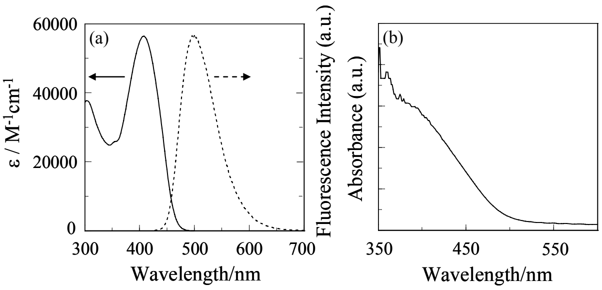


Fig. 1 (a) Absorption (–) and fluorescence (···) spectra of **SAT-1** in THF and (b) absorption spectrum of **SAT-1** adsorbed on TiO_2 film (3 μm).

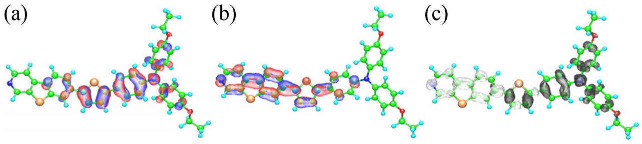


Fig. 2 (a) HOMO and (b) LUMO of **SAT-1**. The red and blue lobes denote the positive and negative phases, respectively, of the coefficients of the MOs. The size of each lobe is proportional to the MO coefficient. (c) Calculated electron density changes accompanying the first electronic excitation of **SAT-1**. The black and white lobes signify the decrease and increase in electron density accompanying the electronic transition, respectively. Their areas indicate the magnitude of the electron density change. (Light blue, green, blue, red, and gold balls correspond to hydrogen, carbon, nitrogen, oxygen, and sulfur atoms, respectively.)

On the other hand, the absorption band of **SAT-1** adsorbed on the TiO_2 film is broadened compared with that in 1,4-dioxane (Fig. 1b). However, the absorption peak wavelength of **SAT-1** adsorbed on TiO_2 is similar to that in 1,4-dioxane. Thus, this result indicates that **SAT-1** forms weak π-stacked aggregates on TiO_2 surface, which has little influence on the absorption spectrum of the dyes adsorbed on TiO_2 surface.

Thus, to elucidate the adsorption states of **SAT-1**, **BTP-H**, **BTP-Cl** and **BTP-T** on TiO_2 nanoparticles, we measured the FTIR spectra of the powders and the compounds adsorbed on TiO_2 nanoparticles (Fig. 3). For the powders of **SAT-1** and the three derivatives, the characteristic stretching bands for C=N or C=C were clearly observed at around 1595 cm^{-1}. In the FTIR spectra of **BTP-H**, **BTP-Cl** and **BTP-T** adsorbed on TiO_2 nanoparticles, the band at around 1595 cm^{-1} disappeared completely, and a new and strong band appeared at 1606 cm^{-1} for **BTP-H**, 1602 cm^{-1} for **BTP-Cl** and 1601 cm^{-1} for **BTP-T**, respectively, which can be assigned to the coordinated pyridyl group to the Lewis acid sites on the TiO_2 surface.[12a–d, 15] Interestingly, when the dye **SAT-1** was adsorbed on the TiO_2 nanoparticles, the stretching band at 1594 cm^{-1} is shifted by 4 cm^{-1} to higher wavenumber, that is, the band at 1598 cm^{-1} can be assigned to the hydrogen-bonded pyridyl group to Brønsted acid sites on the TiO_2 surface.[12a–d, 15] These observations clearly indicate that **BTP-H**, **BTP-Cl** and **BTP-T** are predominantly adsorbed on the TiO_2 surface through coordinate bonding at Lewis acid sites, whereas the dye **SAT-1** is predominantly adsorbed on the TiO_2 surface through the hydrogen bonding at Brønsted acid sites (Fig. 4). Therefore, these results reveal that the formation of coordinate bonding or hydrogen bonding between the pyridyl group of dye and the TiO_2 surface can be controlled by adjusting the electron density on the nitrogen atom of the pyridyl group. Further studies to ensure this conclusion are now in progress by estimating pK_a values of **SAT-1** and the benzo[4,5]thieno[2,3-*c*]pyridine derivatives and will be reported in a subsequent paper.

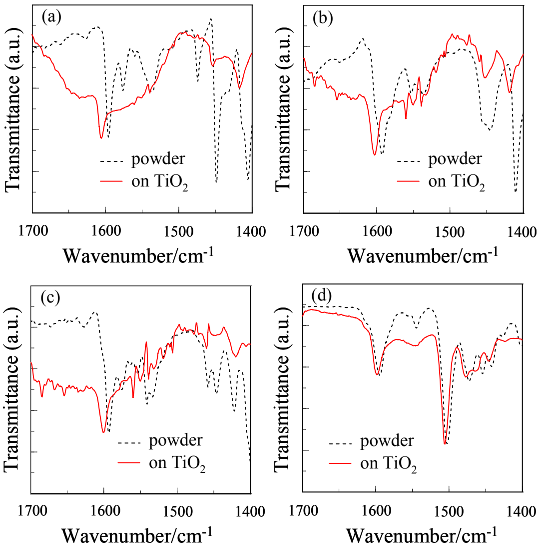


Fig. 3 FTIR spectra of the powders and the compounds adsorbed on TiO_2 nanoparticles for (a) **BTP-H**, (b) **BTP-Cl**, (c) **BTP-T** and (d) **SAT-1**.

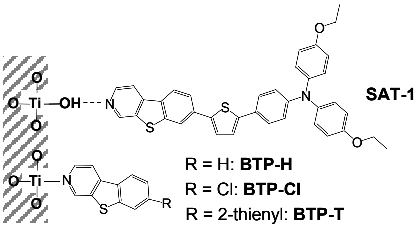


Fig. 4 Configuration of **SAT-1** and benzo[4,5]-thieno[2,3-*c*]pyridine derivatives **BTP-H**, **BTP-Cl** and **BTP-T** on the TiO_2 surface.

The electrochemical properties of **SAT-1** were investigated by cyclic voltammetry (Fig. 5). The reversible oxidation peak was observed at 0.27 V vs. ferrocene/ferrocenium (Fc/Fc^+). The corresponding reduction peak appeared at 0.20 V, thus showing that the oxidized state is stable. The HOMO energy level was evaluated from the half-wave potential for oxidation ($E^{ox}_{1/2}$ = 0.24 V). The HOMO energy level was 0.87 V vs. the normal hydrogen electrode (NHE), thus indicating that the HOMO energy level is more positive than the I_3^-/I^- redox potential (0.4 V). This assures efficient regeneration of the oxidized dyes by electron transfer from the I_3^-/I^- redox couple in the electrolyte. The LUMO energy level was estimated from the $E^{ox}_{1/2}$ and an intersection of absorption and fluorescence spectra (458 nm; 2.71 eV). The LUMO energy level for the dye was –1.84 V, which is higher than the energy level of the CB of TiO_2 (–0.5 V), so that the dye **SAT-1** can efficiently inject electrons to the TiO_2 electrode.

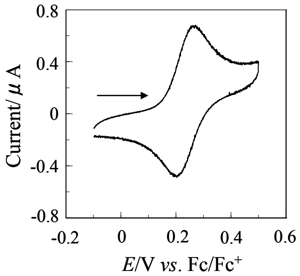


Fig. 5 Cyclic voltammogram of **SAT-1** in acetonitrile containing 0.1 M Bu_4NClO_4 at a scan rate of 100 mV s^{-1}. The arrow denotes the direction of the potential scan.

The DSSC was prepared using the dye-adsorbed TiO_2 electrode (9 µm), Pt-coated glass as a counter electrode, and an acetonitrile solution with iodine (0.05 M), lithium iodide (0.1 M), and 1,2- dimethyl-3-propylimidazolium iodide (0.6 M) as an electrolyte. The photocurrent–voltage (*I*–*V*) characteristics were measured under simulated solar light (AM 1.5, 100 mW cm^{-2}). The incident photon-to-current conversion efficiency (IPCE) spectrum and the *I*–*V* curve are shown in Fig. 6. It is worth mentioning here that the adsorption amount of **SAT-1** adsorbed on TiO_2 electrode is 9.5×10^{16} molecules per cm^2, which is comparable to that of conventional D–π–A dye sensitizers with carboxyl groups. The DSSC based on **SAT-1** gave a solar energy-to-electricity conversion yield (η) of 1.11% with a short-circuit photocurrent density (J_{sc}) of 3.12 mA cm^{-2}, a open-circuit photovoltage (V_{oc}) value of 548 mV, and a fill factor (*ff*) of 0.67. The maximum IPCE value reaches 40 % at 428 nm, but it is lower than those of D-π-A dyes with pyridyl group possessing a high coordinate bonding ability to Lewis acid sites on the TiO_2 surface.[12a, b] Thus, these results reveal that the formation of hydrogen bonding between the pyridyl group of dye and the Brønsted acid sites on the TiO_2 surface results in less efficient electron injection than the formation of coordinate bonding between the pyridyl group of dye and the Lewis acid sites on TiO_2 surface.

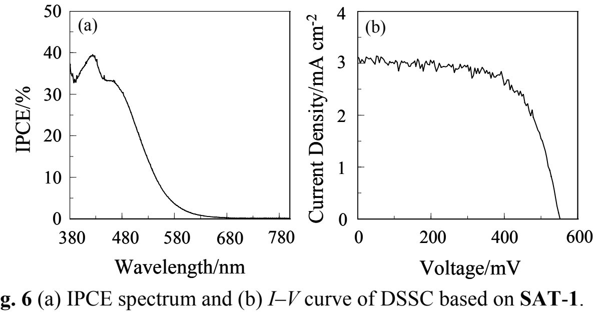


Fig. 6 (a) IPCE spectrum and (b) *I–V* curve of DSSC based on **SAT-1**.

In conclusion, as a new type of D–π–A dye sensitizer for DSSCs, we have designed and synthesized **SAT-1** with thiophene-fused pyridine ring, benzo[4,5]thieno[2,3-*c*]pyridine as electron-withdrawing–anchoring group. It was found that benzo[4,5]thieno[2,3-*c*]pyridine derivatives are predominantly adsorbed on the TiO_2 surface through coordinate bonding at Lewis acid sites, whereas **SAT-1** is predominantly adsorbed on the TiO_2 surface through the hydrogen bonding at Brønsted acid sites. Thus, we demonstrated that the formation of coordinate bonding or hydrogen bonding can be controlled by adjusting the electron density on the nitrogen atom of the pyridyl group. This work indicates that the formation of hydrogen bonding between the pyridyl group of dye and the Brønsted acid sites on the TiO_2 surface is unfavorable for the electron injection, compared with the formation of coordinate bonding between the pyridyl group of dye and the Lewis acid sites on TiO_2 surface.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Details of experimental procedures, synthesis and characterization of compound. See DOI: 10.1039/b000000x/

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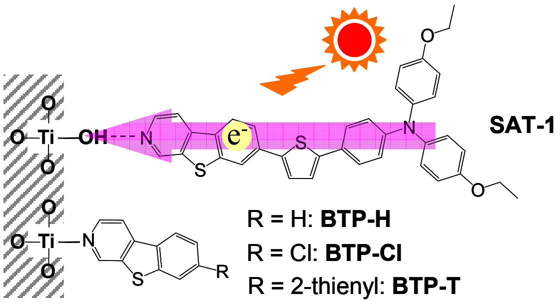
Graphical abstract:



D-π-A dye **SAT-1** with benzo[4,5]thieno[2,3-*c*]pyridine as electron-withdrawing anchoring group capable of forming a hydrogen bonding at the Brønsted acid sites or a coordinate bonding at the Lewis acid sites on TiO_2 surface was designed and developed as a new-type of D-π-A dye sensitizer for dye-sensitized solar cells.